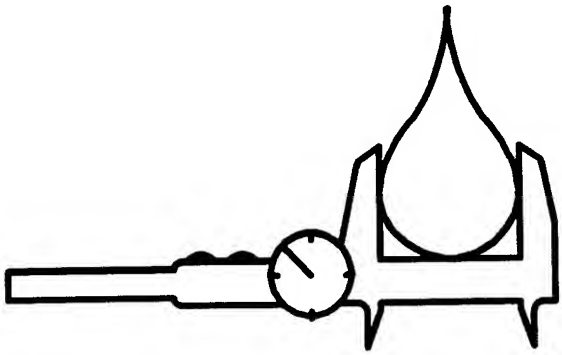
Fast Response Sensor for the Measurement of the Optical Properties and Carbon Content of Organic Aerosols

Final Report, May 1-October 31, 2000
Contract N00244-00-P-2504
Navy Small Business Innovation Research Program
Office of Naval Research

DROPLET MEASUREMENT TECHNOLOGIES



P.O. Box 20293
Boulder, Colorado 80308
Phone: 303.440.5576
Fax: 303.440.1965
ceo@dropletmeasurement.com
http://www.dropletmeasurement.com

Approved for public release; distribution unlimited

Abstract

This report was developed under an SBIR contract for Solicitation Topic N00-094. In this study a protoype instrument, the aerosol vaporization spectrometer (AVS) was evaluated for the ability to classify particles by their incandescent signal. The objective is to provide real-time mass information on airborne black carbon particles. The instrument uses a diode pumped Nd:YAG laser at 1.06 μ wavelength to excite the particles. The scattering signal is monitored from all of the particles, and the black carbon particles absorb sufficient energy to incandesce, and this incandescence is measured by broadband and narrowband detectors. Two type of carbon particles were tested, those generated from an electric spark between graphite rods, and the nebulization of colloidial graphite particles. These studies indicate the feasibility of this technique to measure particulate black carbon particles down to 100 nm . From the ratio of the scattering to incandescence signals, it appears possible to obtain information on the shape of the particles, gaining information on the surface to volume ratio.

1.0 Overview

This report summarizes activities on the "Fast Response Sensor for the Measurement of the Optical Properties and Carbon Content of Organic Aerosols", under the Navy contract N00244-00-P-2504. This is an SBIR Phase I project whose objective is the study of an instrument that will provide the mass of single, black carbon particles. The goal is to evaluate a prototype instrument, the aerosol vaporization spectrometer (AVS), that uses a patented sensing technique to classify particles by their incandescent signals.

In the first month of the project, May, 2000, the AVS was transported from Research Electro-Optics (REO), the company that developed the AVS technique, to the DMT laboratory. There it was installed, cleaned, and aligned by REO and DMT personnel and prepared for the calibration studies. The optical configuration is shown in the block diagram in Fig. 1. During the second month, graphitic carbon particles were generated with a nebulizer from particles in a liquid solution and also with a spark generator. The particles were selectively sorted by size using an electrostatic classifier and introduced into the sample cavity of the AVS where their scattered and incandesced light was detected. The signals from the three detectors was digitized and stored for subsequent analysis. The focus of the third month activities was on the data processing and analysis of the measurements made in June. This entailed preparation of data files by correcting for signal offsets, generating signal statistics, e.g., averages, standard deviations, minimum and maximums, etc., and calculating signal characteristics, e.g. peak height, pulse width and area, rise and fall times, etc. In the fourth month of the SBIR the size and mass of particles measured with the AVS were quantified and a sensitivity analysis determined that the carbon mass could be determined using a combination of peak scattered light from the visible light detector combined with the area of pulses generated from the infrared detector. The temperature of incandescence was validated by looking at the theoretically calculated black body temperature compared to the measured signals from detectors with filters selecting a different range of wavelengths.

The remainder of this report highlights the major findings from this study and discusses the plans for Phase II evaluations and hardware developments.

Exhibit A

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	10-31-2000	Final 05-01-2000 to 10-31-2000

4. TITLE AND SUBTITLE
Fast Response Sensor for the Measurement of the Optical Properties and Carbon Content of Organic Aerosols

5. FUNDING NUMBERS
N00244-00-P2504

6. AUTHOR(S)
Darrel Baumgardner

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Droplet Measurement Technologies
2400 Central Avenue, Suite A, Boulder, Colorado 80301

8. PERFROMING ORGANIZATION REPORT NUMBER
NCC-1-1

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research, Regional Contracts Dept, Code 260
937 Harbor Drive
Sand Diego, California 92132-0212

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approval for public release; distribution unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

In this study a protoype instrument, the aerosol vaporization spectrometer (AVS) was evaluated for the ability to classify particles by their incandescent signal. The objective is to provide real-time mass information on airborne black carbon particles. The instrument uses a diode pumped Nd:YAG laser at 1.06 μ wavelength to excite the particles. The scattering signal is monitored from all of the particles, and black carbon particles absorb sufficient energy to incandesce, and this incandescence is measured by broadband and narrowband detectors. Two type of carbon particles were tested, those generated from an electric spark between graphite rods, and the nebulization of colloidial graphite particles. These studies indicate the feasibility of this technique to measure particulate black carbon particles down to 100 nm . From the ratio of the scattering to incandescence signals, it appears possible to obtain information on the shape of the particles, gaining information on the surface to volume ratio.

14. SUBJECT TERMS
Black carbon, analysis, laser incandescence

15. NUMBER OF PAGES 24

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
unclassified	unclassified	unclassified	UU

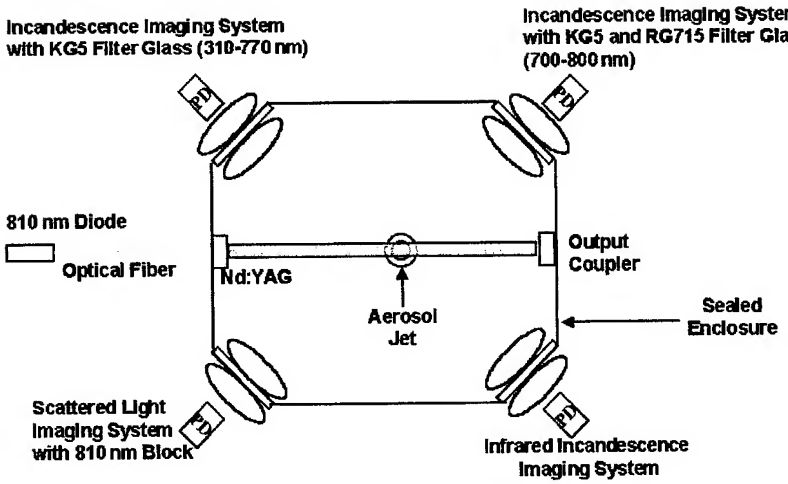


Figure 1
Block diagram showing basic optical components of the AVS

2.0 Major Findings

The five questions that were to be addressed in the Phase I proposal were the following:

1) How accurately can soot mass be derived?
2) What is the minimum detection limit?
3) What is the maximum particle sample rate?
4) What are the optimal wavelengths for determining particle composition?
5) How well can the response of the AVS be modeled?

The first four questions have been addressed through a combination of modeling and observational studies, summarized in the sections 2.1-2.4. In addition, another feature of this measurement system was revealed during the observational studies that expands the capability of the AVS for determining particle structure. This feature is described in section 2.5. A more complete theoretical model of the AVS is in progress but could not be completed by the end of the Phase I contract.

2.1 Accuracy of determining soot mass

The theory predicts that absorbing particles, as they enter the focal point of the laser beam, will first scatter light according to Mie scattering theory and be detected by the detector that measures light only at a wavelength of 1.06 μm, the wavelength of the laser. As the particle absorbs this radiation, it will rapidly heat to the point of

vaporization and producing visible light by incandescence. This light is detected by two detectors that are filtered in the wavelength bands of .310 - .770 μm and .700-.800 μm, respectively. As the particle vaporizes, the scattered light will decrease rapidly and the incandescence light will continue until the majority of particle mass is converted to vapor. The laboratory tests show this response of the detectors, as illustrated in Figure 2 for calibration particles (graphitic carbon) of three different sizes. In this figure is seen that the scattering signal appears first, followed by the incandescent signals several microseconds later. As predicted, the scattering signal decreases and disappears more rapidly than the incandescent signals that have a long tail as the particle vaporizes. The amplitude of scattering signal is a measure of the particle size and the peaks of the incandescence signals are a measure of the particle mass.

Studies relating the AVS response to carbon particle mass were conducting using carbon particles from two types of particle generators. Carbon particles were produced with a commercial generator that produces a spark discharge between two graphite rods, from which graphite agglomerates between 50 and 200 nm are produced, according to the manufacturer . The second system for generating particles was with a solution of graphite particles and water. The graphite particles were in the form of a powder called Aquadag by the manufacturer. The solution of Aquadag and water were put in a nebulizer and formed a spray. In both calibration techniques, the output of the generators were brought through an electrostatic classifier to select a particular size range that was introduced to the AVS. In the case of the spark generated particles, the residence time between generation and size selection is fairly less than 5 seconds, leaving little time for the aggregates to collapse into more compact form. The electrostatic sizer is sensitive to the aerodynamic size, i.e. the surface equivalent size. It is very likely that the spark generated particles have complex structures with a high surface to volume ratio that make estimating either their size or mass difficult. On the other hand, the Aquadag particles are disc shaped. The crystal structure is shown in Figure 3, and particles form when the material cleaves in sheets along horizontal axis in Figure 3. The lubricating properties of graphite are due to the particles sliding over each other. Information on the diameter to thickness ratio is not known but we have assumed a 5:1 ratio in our calculations of volume and mass.

Figure 4 shows the peak response of the scattering detector to the two types of calibration particles. The diameter reported on the abscissa is the nominal value set on the electrostatic classifier. The horizontal error bars are estimates of the uncertainty in size based upon the assumption that the particles are not spherical. As discussed above, the uncertainty in size could be quite large in the case of the spark generated particles. The vertical error bars are standard deviations about the average maximum amplitude of a number of signal traces at each particle size. As can be seen when comparing the two figures, for the same nominal particle sizes the peak heights are almost three times large for the Aquadag as for the spark generated particles. The second thing to be seen is that the response is much flatter for the spark generated particles than for the Aquadag. From these observations we concluded that the particles from the spark generator were too irregular to be used for calibration purposes and these measurements were not analyzed

further, with the exception of evaluating the two-color pyrometery response and the peak to area ratios to examine particle structure.

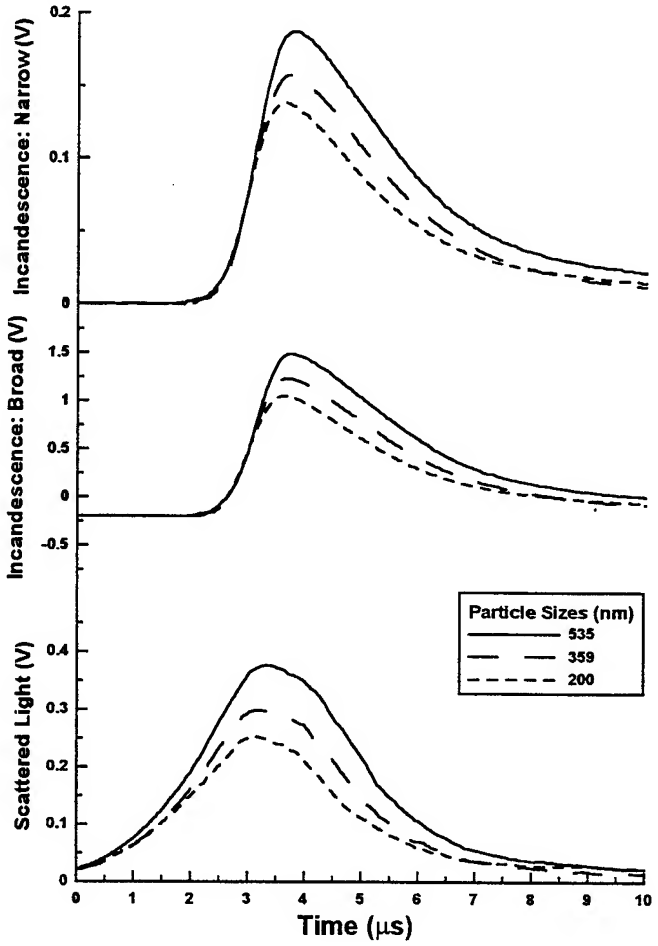


Figure 2

Representative time traces from the three detectors of the AVS: Scattering signal (bottom panel), broad band incandescent signal (middle panel) and narrow band incandescent signal (top panel) for three different particle sizes.

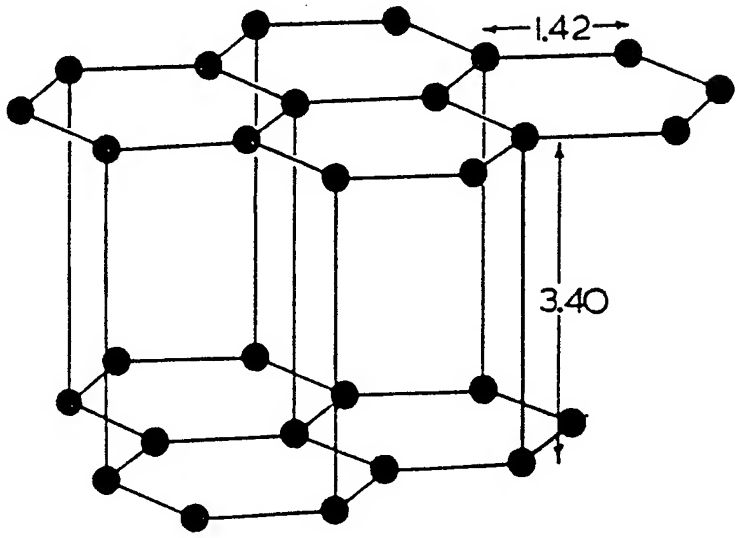


Figure 3

Crystal structure of carbon in the graphite form. The bond dimensions are given in Angstroms.

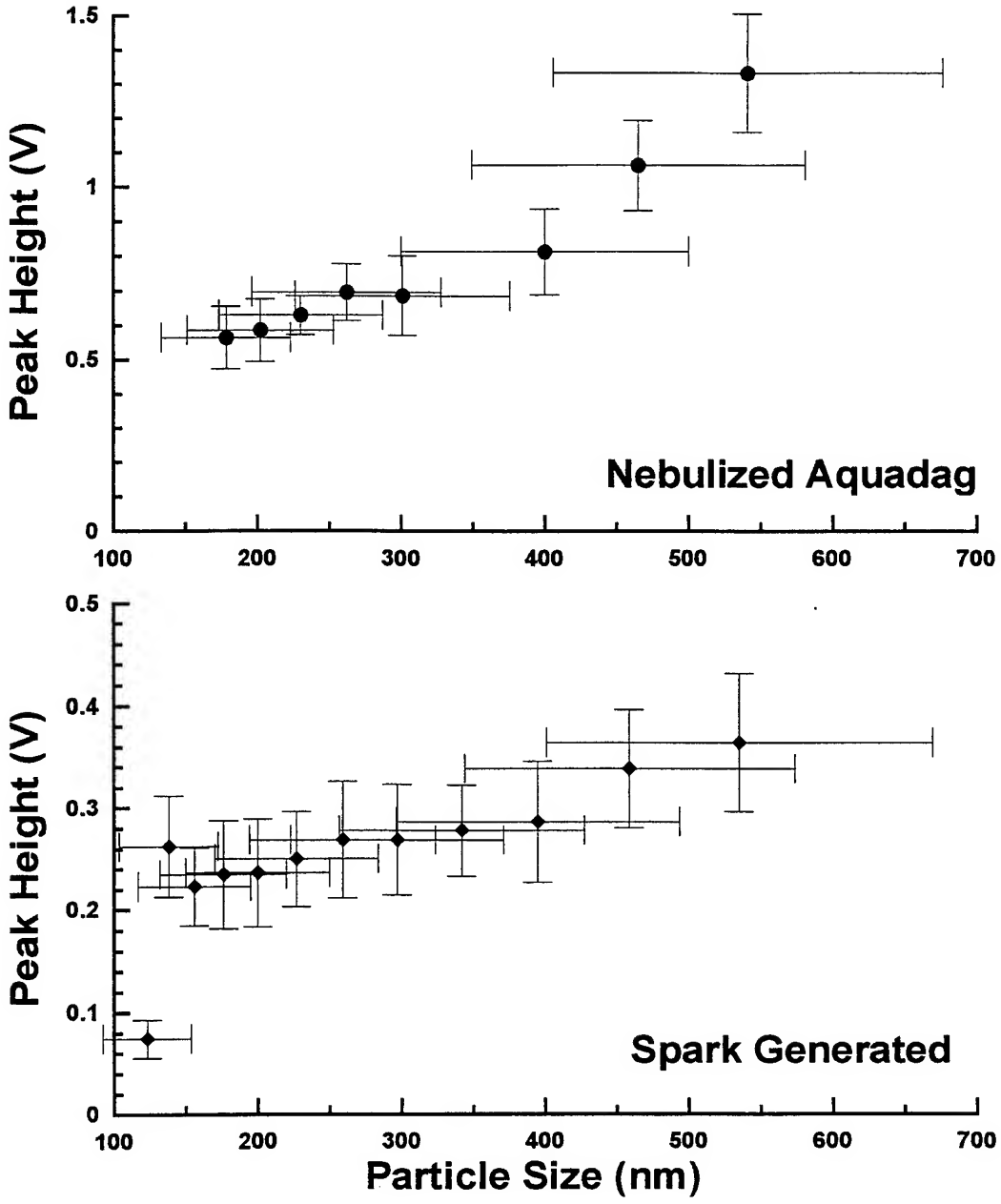


Figure 4

Peak scattering signal versus nominal electrostatic classifier size for spark generated particles (bottom panel) and Aquadag (top panel).

Figures 5 and 6 show the response of the broadband incandescence detector as a function of particle size and mass, respectively. The bottom panel of each figure is the average peak response and the top panel the area of the signal trace. These are only for the Aquadag particles. The horizontal error bars are estimates of uncertainty and the vertical bars are the standard deviations about the averages. The largest uncertainties stem from the sizing uncertainty of the electrostatic sizer, and the unknown diameter to thickness ratio of the particles. Both of these uncertainties can be decreased once more information is obtained from the manufacturer about structure of the particles. The relatively small standard deviations about the average peaks and areas, however, indicate that the particle to particle deviation is relatively small and a better calibration curve could be obtained with more knowledge about the particle shape. This will be a central focus of Phase II activities.

The curves in the four figures are power-law best fits where the proportion between Y and X is shown in each figure. Both the signal peaks and areas are sensitive to the particle mass and follow a power law relationship. The important thing to note, however, is that in this size range, the signal peak scales as mass to the 0.19 power, whereas signal area scales as mass to the 0.26 power. This is important for two reasons. Using signal area instead of signal peak increases the signal to noise ratio. Secondly, the higher sensitivity of the signal area to mass provides better resolution when deriving particle mass.

The Phase I studies did not provide the hoped for determination of accuracy, but sufficient information was obtained to observe that the system responded as expected from the theoretical considerations and that an improvement in the calibration system will significantly decrease the error bars.

2.2 Minimum Detection limit

The smallest particles used in the Aquadag studies were 0.176 um. These were not small enough to test the minimum detectable size/mass of the AVS. Phase II studies, with particles of more uniform shape, will be used to establish these minimum thresholds in the laboratory. Prior to these studies however, we have estimated the minimum sizes that can be detected by the scattering and incandescent detectors using theoretical models. Figure 7 shows a comparison between the peak scattering signals observed and those predicted using Mie scattering theory under the assumption of spherical particles with an index of refraction of 1.76 - .440i, a collection angle from 120-150 degrees and laser wavelength of 1.06 μm. It can be seen that the agreement is not particularly good, as the particles that were measured were not spherical and a fair amount of uncertainty exists in their size. In addition, it can be seen that this size range has an unfortunate oscillation where the response is rather flat in the size range of interest. As will be discussed below, this problem will be addressed in the Phase II developments. Nevertheless, the general trends are about the same and an examination of the theoretical curve allows us to estimate the minimum size that one could expect to see with the scattering detector. The average noise level that was measured from the scattering

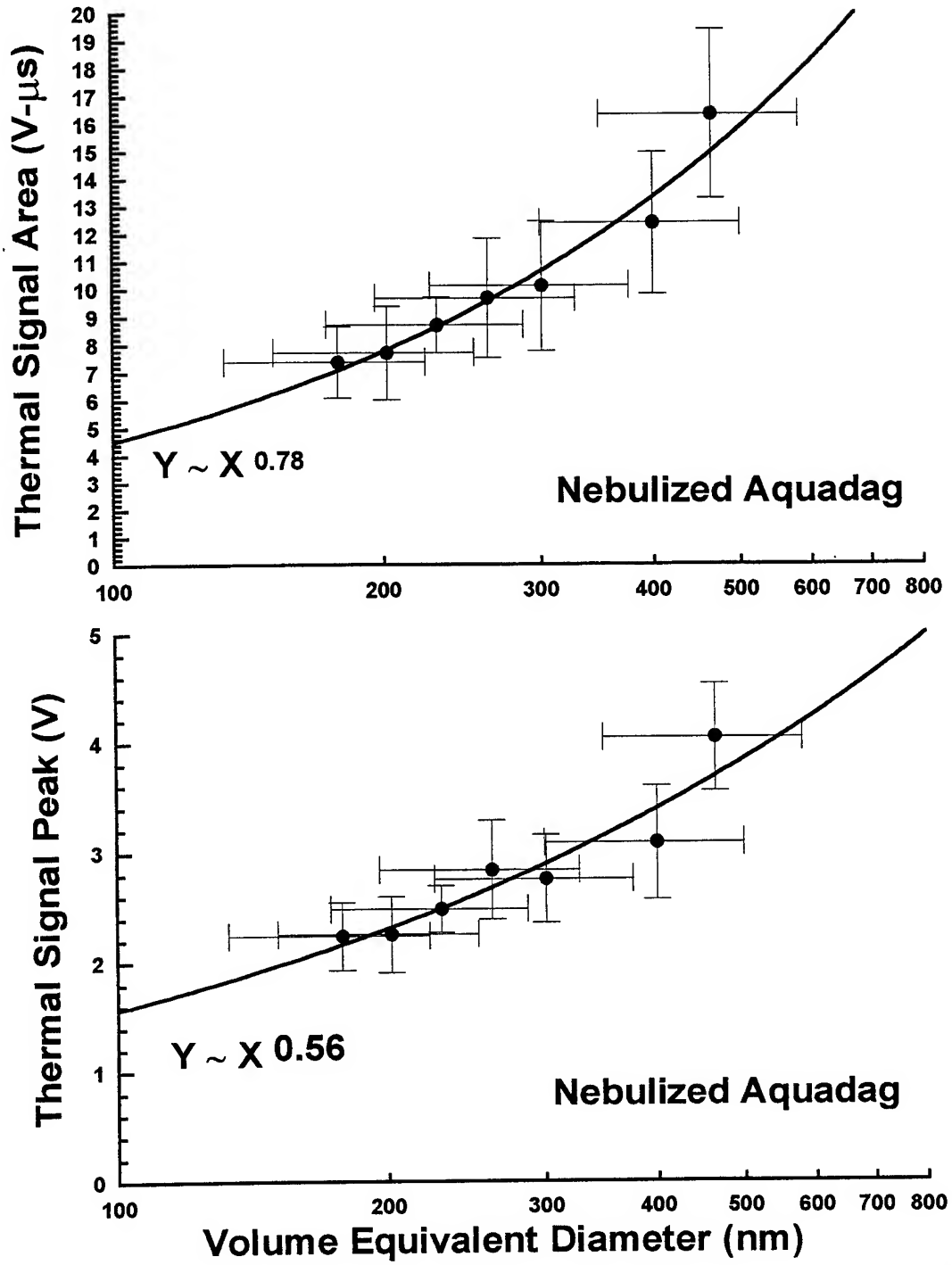


Figure 5

Response of broadband incandescence detector as a function of particle diameter. The top panel is area of the signal and the bottom panel is the peak response. The curve is the best fit power law with the relationship between X and Y given.

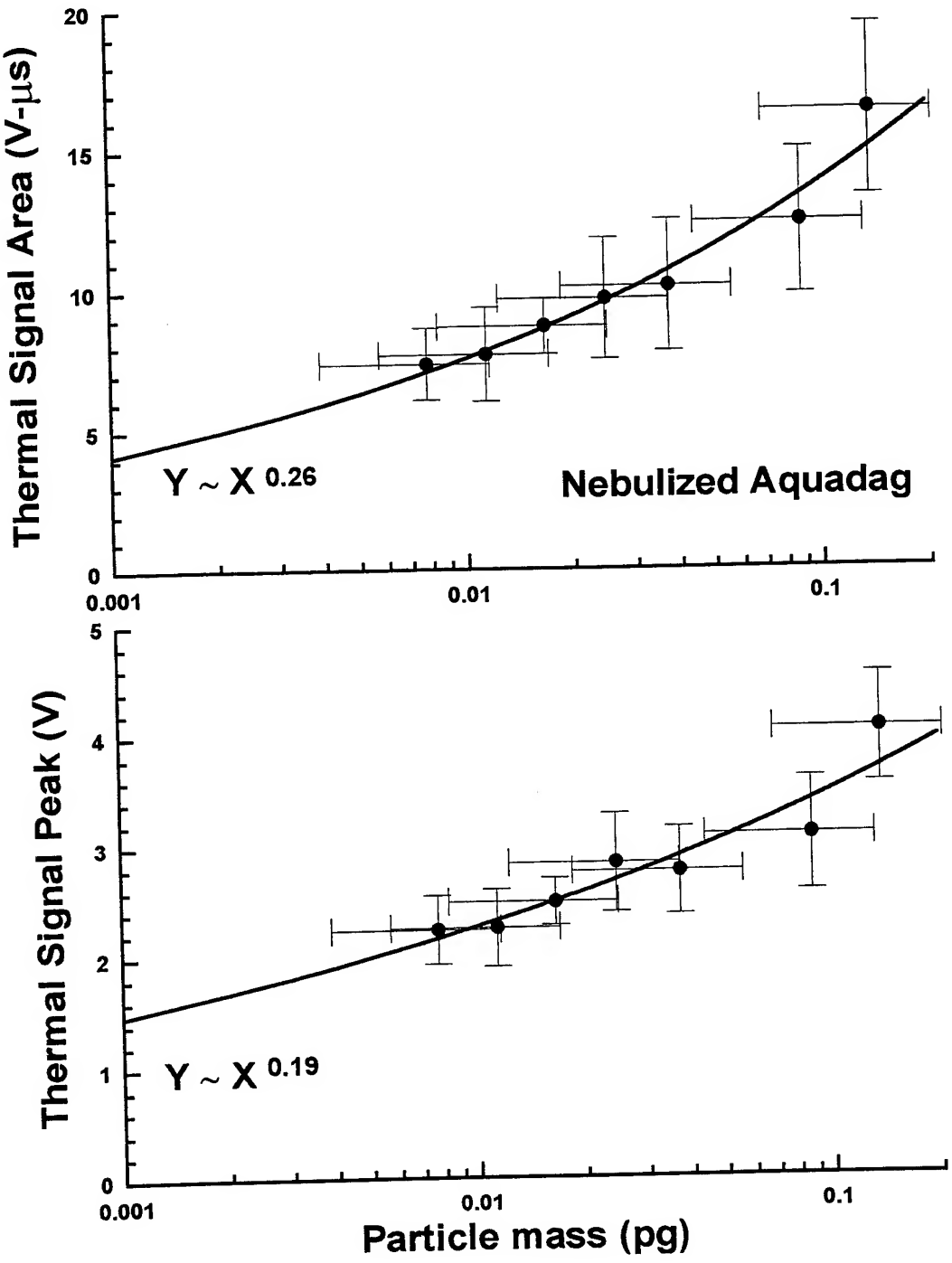


Figure 6

Response of broadband incandescence detector as a function of particle mass. The top panel is area of the signal and the bottom panel is the peak response. The curve is the best fit power law with the relationship between X and Y given.

detector was 10 mV. Looking at Fig. 7, we can see that at 100 nm particle size, the theoretical signal is about twice this level. Hence, it should be possible to detect 100 nm particles with this system in its current optical configuration.

The minimum size detectable by the incandescent detector is estimated by equating the predicted signal with the detector noise level. A simple model for the energy emitted by an incandescing particle is:

$$E_I = d\Omega\Delta\eta\sigma_{sb}T^4 4\pi a^2\varepsilon$$

where $d\Omega$ is the fraction of light collected by the imaging system, Δ is the fraction of incandescent light emitted over the spectral region of the detector, η is the response of the detector, σsb is the Stefan-Boltzmann constant, T is the particle boiling point, a is the particle radius, and ε is the emissivity of the spectral region that the incandescence signal is detected. The detector noise level, E_N, is given by

$$E_N = f(N^2 + I_N^2)^{1/2}$$

where f is the detector bandwidth, N is the detector amplifier noise current, and I_N is the photodetector noise current. Setting E_I equal to E_N and solving for the radius, a, we can estimate the minimum size when the emitted energy is equal to the energy of the noise, i.e. a signal to noise ratio of 1. Figure 8 shows how this minimum size varies with temperature of incandescence and the fraction of light collected over the spectral range of the broadband incandescent channel. The values for electronic noise levels were obtained from REO, the collected light fraction is for the current optical configuration, and the present filter arrangement provides for a collection of 0.3 of the emitted light over the spectral range. The curves at .4 and .5 fractions demonstrate how the minimum size could be lowered by increasing the spectral width of the filters.

For the current optical arrangement and selection of electronic components, the estimated minimum size that could be detected at 4000 K, the incandescent temperature of carbon, is approximately 80 nm. This remains to be verified, however, with careful laboratory studies.

2.3 Maximum particle rate.

The only limiting factor in the AVS that set the upper particle rate is the width of the laser beam. Digital electronics are more than fast enough these days to process the signals from individual particles in the intervening time between events. Even in the worst case scenario of urban pollution where total particle concentrations can exceed 50000 cm^{-3}, this is an average of 20 μs between particles. As the signal processing will be on-the-fly, i.e. areas and peaks will be calculated while the particle is still in the laser beam, even with Poissonian distributions, very little time will be need to process the particles. The minimum distance between particles will be determined by the width of the laser beam, in this case about 500 μm. The probability that two particle will coincide in

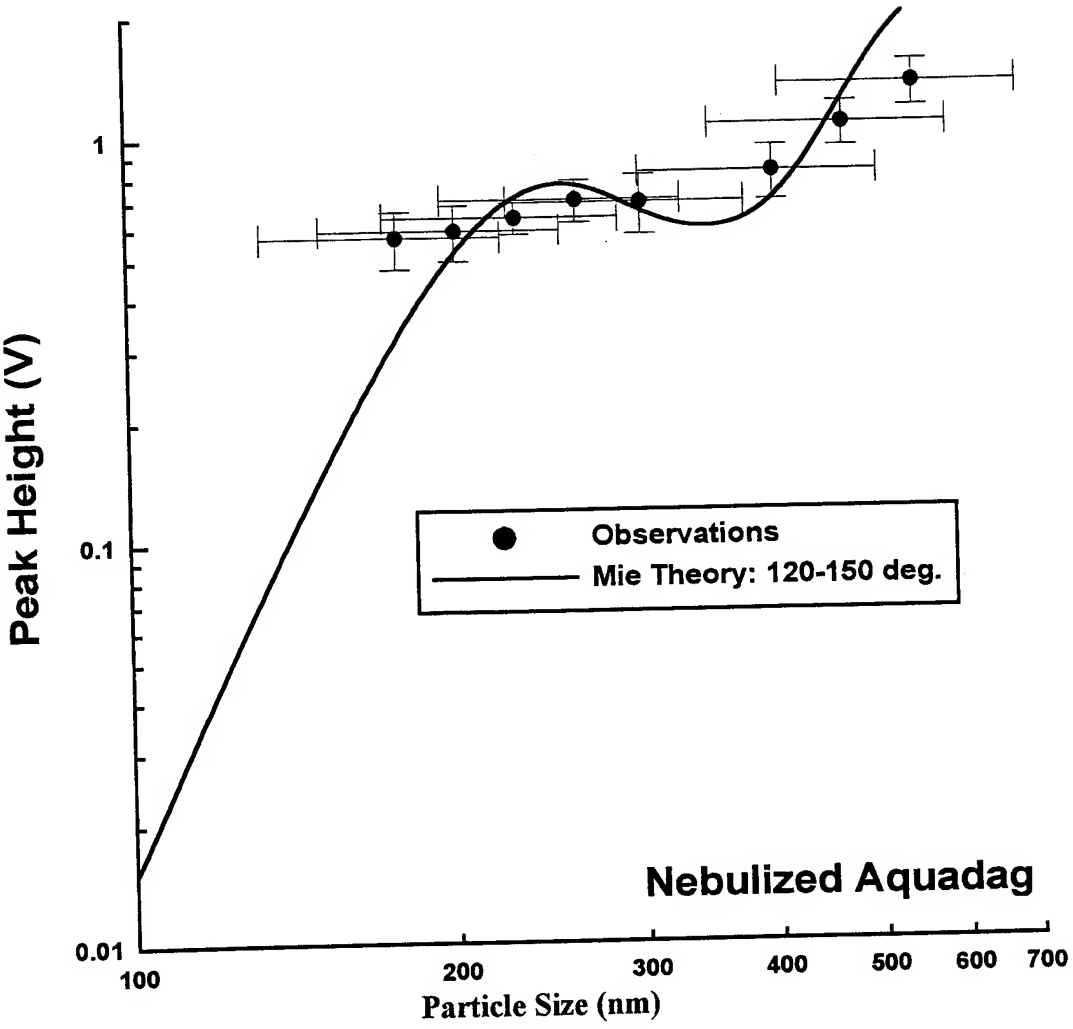


Figure 7

Comparison between peak scattering intensity and Mie scattering theory.

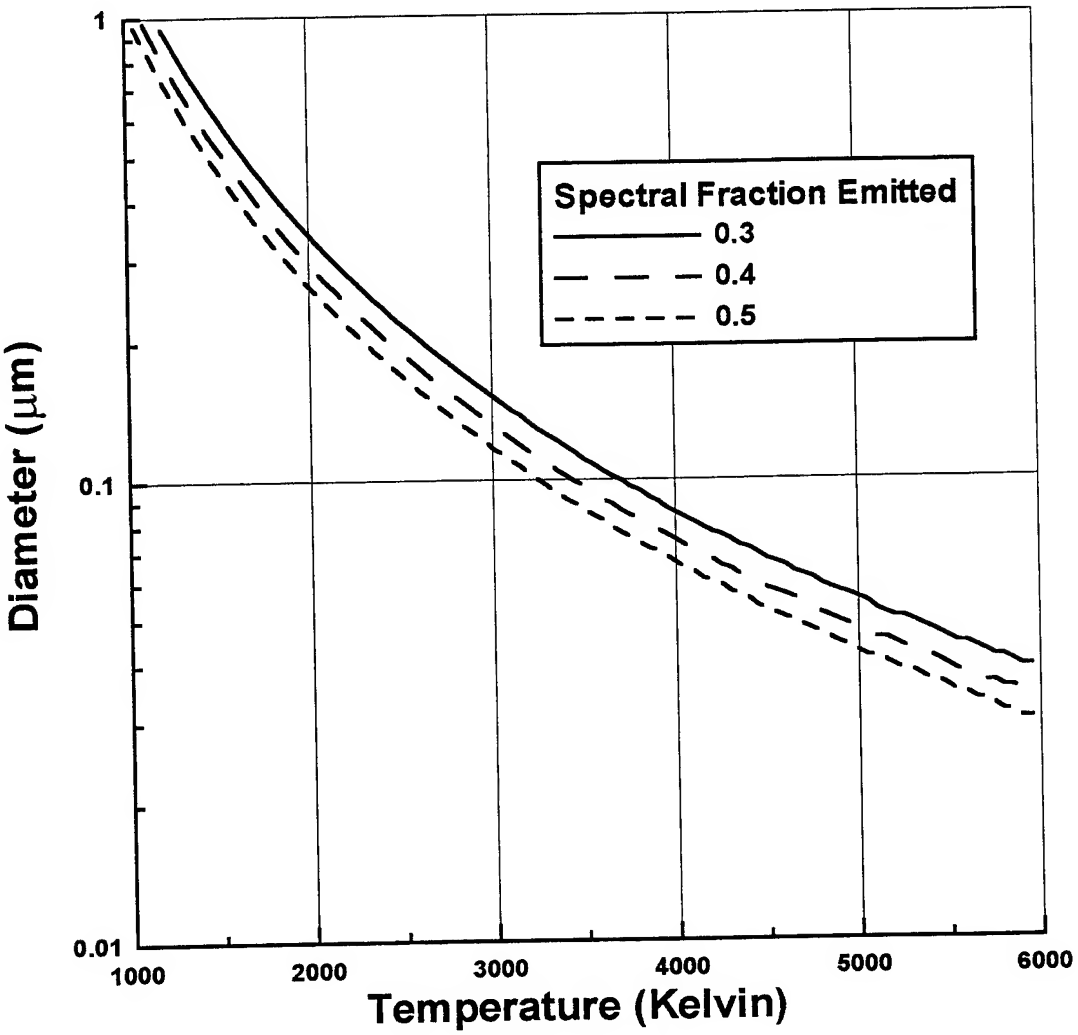


Figure 8

Theoretical variation in the minimum size that can be measured by incandescence as a function of incandescence temperature and the fraction of light collected. The limiting factor used was the detector noise level.

the beam is approximately 10% at a concentration of 10,000 cm^{-3}. This estimate assumes that the particle are uniformly, random distributions in space.

2.4 Composition Determination

The AVS was designed to determine particle composition using two-color pyrometry. The theory is that the amount of black body radiation emitted by a particle is a function of its temperature and emissivity. If a particle's emissivity is known, then the temperature can be estimated by the amount of radiated light at any given wavelength. If this radiation is measured at two wavelengths, then it is not necessary to know the emissivity, as the ratio of the two radiances will be strictly a function of the temperature. The theoretical response of the two detectors was derived for the two incandescence channels and shown in Figure 9 as a ratio of the two channels as a function of temperature. Also shown is the fraction of total emitted light over the spectral range that is collected by the broad band incandescence detector. Figure 10 shows the measured ratios of the two channels. Comparison of the theory with the measurements show that the average ratio of about 9 is within the temperature range for incandescence of carbon particles of 4000 K.

2.5 Particle shape information

An unexpected result of these studies was the discovery that some information about particle shape could be derived from the measurements. From Mie scattering theory, we know that the scattering signal is a function of a particle's surface area, whereas the incandescent signal will be related to the particle volume. Figure 11 shows the result of comparing these two signals for both the spark and nebulizer generated particles. The respective slopes are 5.2 and 3.9 between the incandescence and scattering detector peaks. The slope are an indicator of the relative volume to surface ratio. The two things to note are that the slopes are quite different, as would be expected for particles with different shapes. Secondly, the correlation between the two independent signals are highly correlated and very linear, indicating that within the sample populations, the shapes maintain similar forms, regardless of their size. Further investigations will provide additional information on the value of this ratio for determining particle shapes.

3.0 Phase II Plans

As a result of the Phase I evaluations, the AVS appears to be a highly promising technique that will be a valuable instrument for making measurements of size differentiated carbon mass. The AVS was tested with particles as small as 0.176 μm and the theoretical model suggests that particles smaller than 0.1 μm can be measured from just the scattered light signal. Currently the only commercial optical particle counter (OPC) capable of measuring to smaller sizes is the PMS LAS-X that is advertised to measure down to 0.07 μm. An analysis of the AVS detectors and associated electronics show that it can detect particles as small as 0.08 μm and still be above the noise level.
The goal of the Phase II activities will be to develop an instrument that measures smaller sizes than obtainable with commercially available OPCs and that provides additional

information on particle mass, shape and composition—something that no currently available instrument can provide.

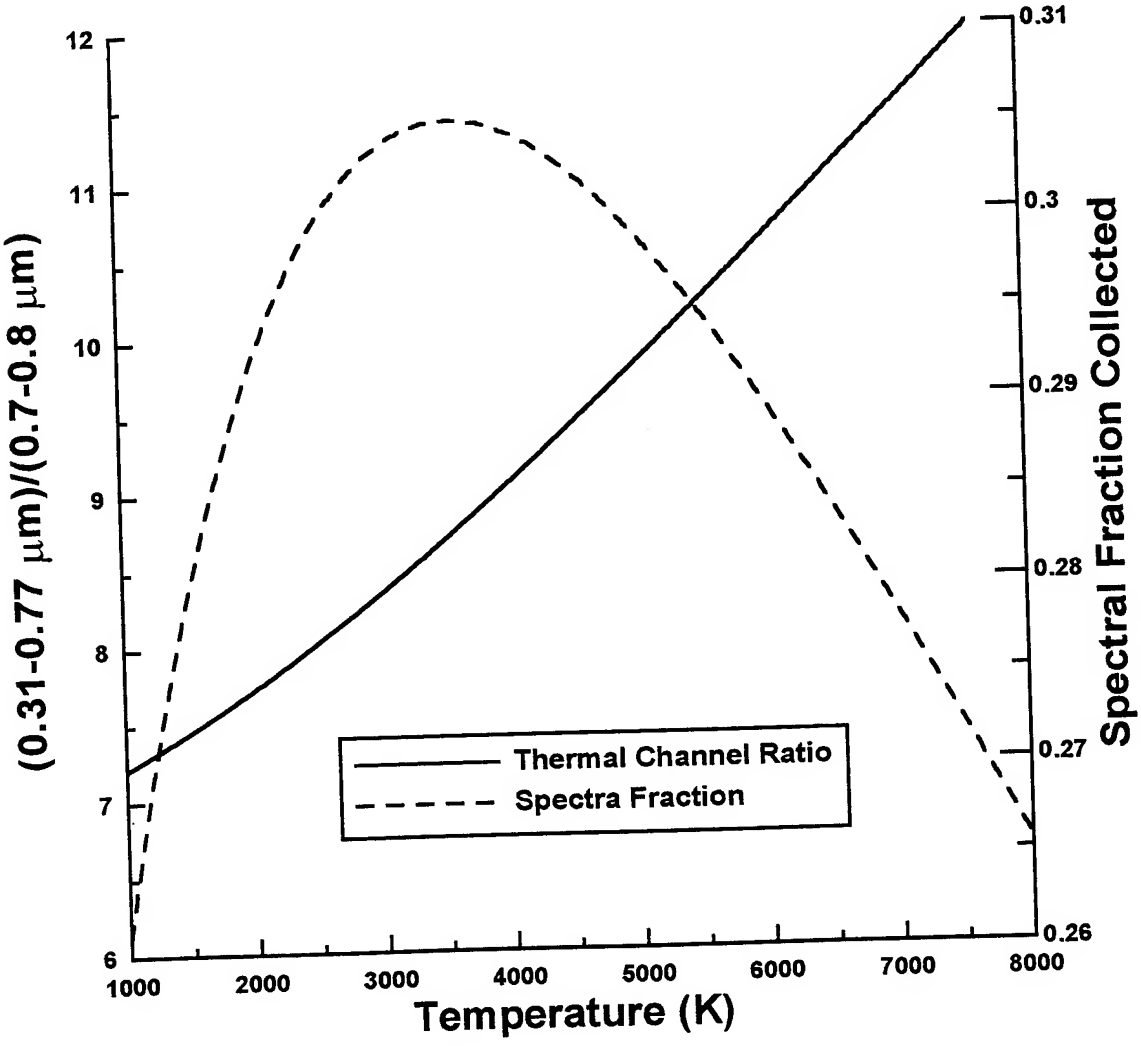


Figure 9

Theoretical ratio of response for the broadband (0.31-0.77 μm) *vs.* narrowband (0.70-0.77 μm) incandescence detectors in the solid curve. The dashed curve shows the total fraction of emission in the broadband wavelength.

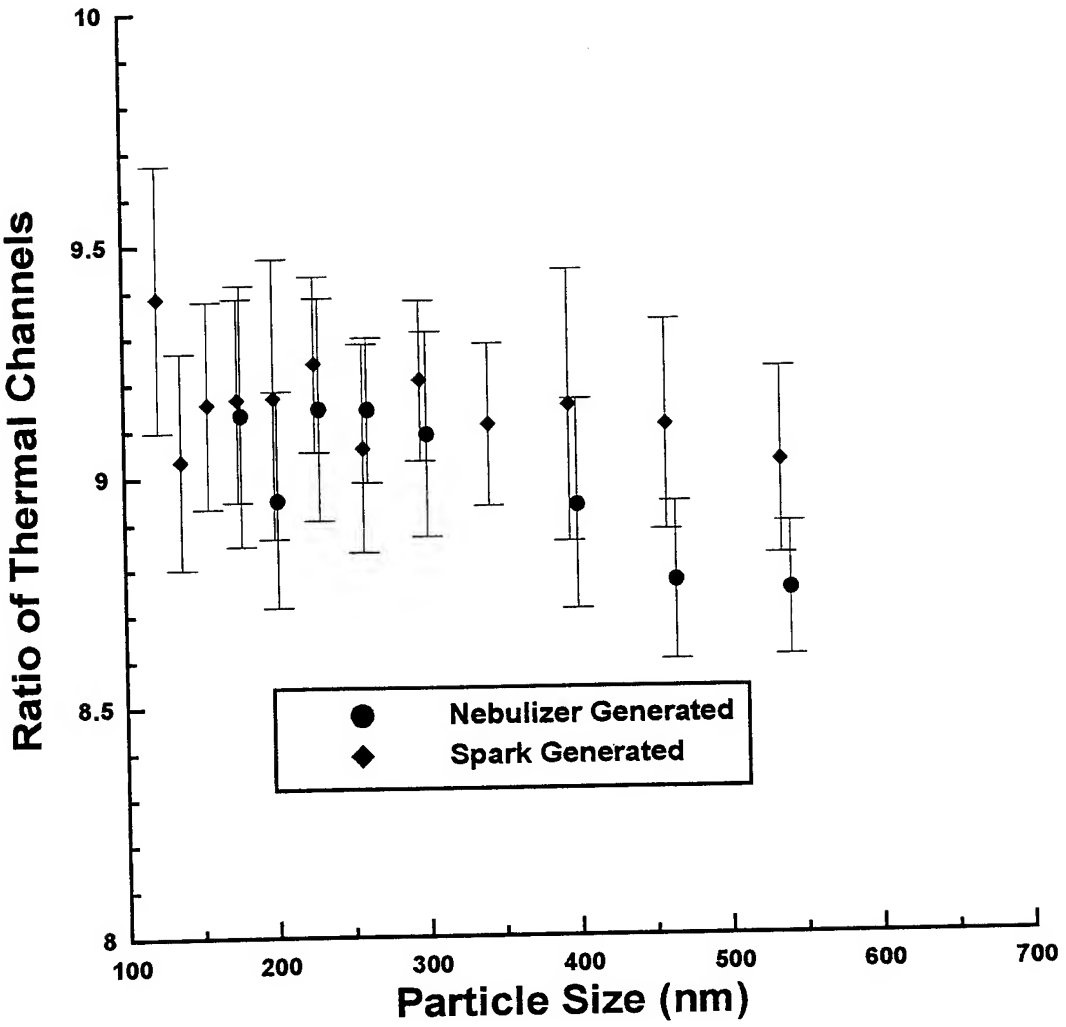


Figure 10

Measured ratio of emission in the broadband and narrowband region for both the nebulizer generated Aquadag and spark generated carbon particles.

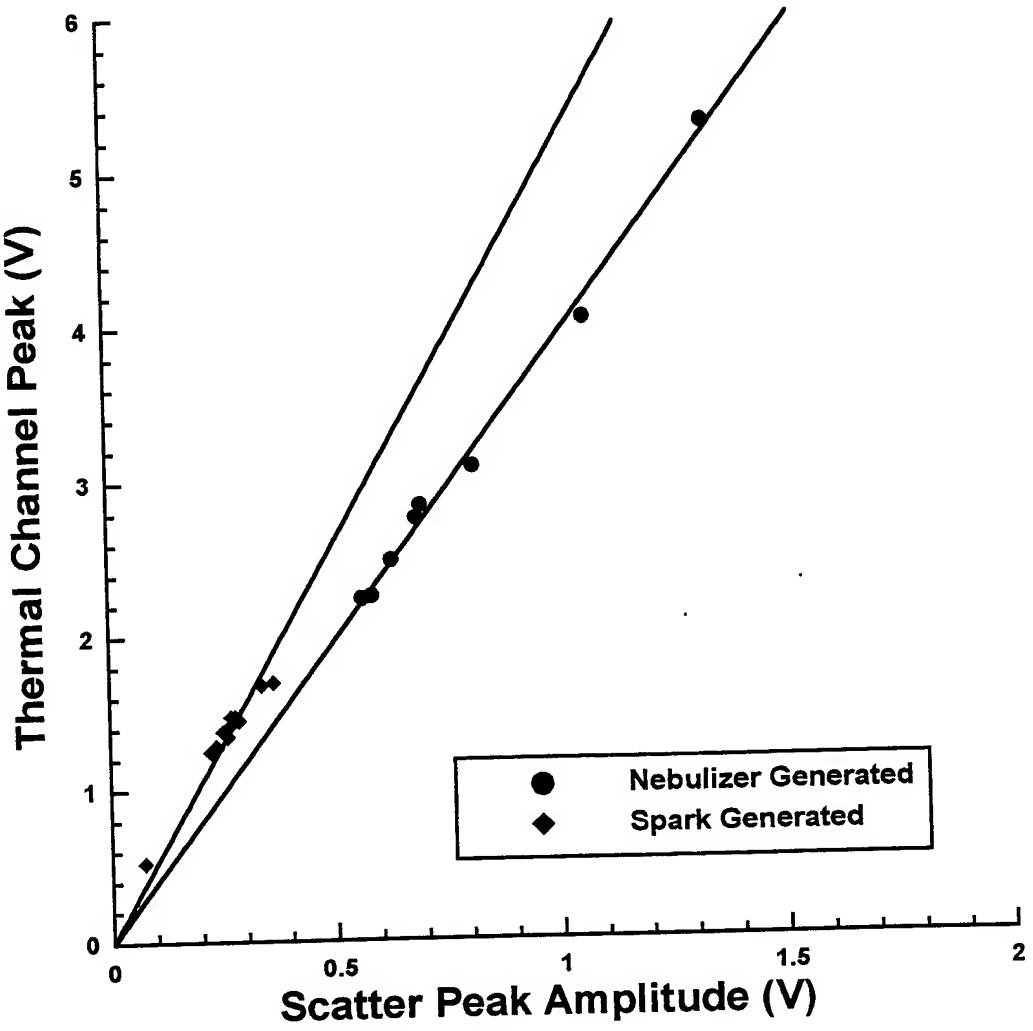


Figure 11

Ratio of scattering to incandescence signals for nebulizer generated Aquadag graphite and spark generated carbon particles. This indicates that the ratio of these two signals can be used to produce information on the particle shape.

additional information on particle mass, shape, and composition – something that no currently available instrument can provide.

The Phase II activities will consist of the following:

3.1 Calibration/Validation System

An essential component of this system is a calibration system that will produce particles of known composition and size. This system will be a combination of a particle

generator followed by an electrostatic classifier with well-characterized performance. We are currently discussing the development of calibration particles with Duke Scientific, a well known manufacture of calibration standards for particle measurements. The intent is to obtain spherical particles, with known absorption coefficient and density. If carbon particles can be generated with these specifications this will be ideal, but a calibration curve established with other light absorbing particles will be sufficient to characterize the system and validate the performance model currently being developed. One particularly good source of such particles will be various metal compounds, as they are relatively easy to produce in spherical shapes and their physical and optical properties are well known.

3.2 Optical bench development

The optical bench that was used in the testing of the AVS was a prototype model that is not well configured for use in the field. The laser and detectors that were used are now several years old and newer systems are now available with higher power and greater sensitivity, respectively. In addition, the angular placement of detectors is not optimal for a field unit and re-engineering will be done to streamline and stabilize the system for less sensitive alignment and more portability. We would also like to increase the sensitivity of the scattered light detector by increasing the collection angles. This will be done by using the same technique currently implemented n the PMS PCASP probe that uses an arrangement of Mangin mirrors to collect light from 35° to 120°. This will increase the collected light by almost a factor of three or more, as shown in Figures 12 and 13. Figure 12 compares the theoretical scattering cross sections, as a function of size for carbon particles, for the current arrangement and a mangin mirror configuration. Figure 13 shows the expected response when the two curves are normalized using the voltage to light intensity response that was shown in Figure 7. This predicts a lower threshold of about 80 nm as the minimum particle size that could be measured with the new optical arrangement.

Tuning of the ND:YAG laser at this point is very difficult after the windows have been cleaned. It appears feasible to make an integrated laser assembly the can fit into the AVS housing and be removed and cleaned in one assembly. This will be an important step in the commercialization of the unit for easier user servicing.

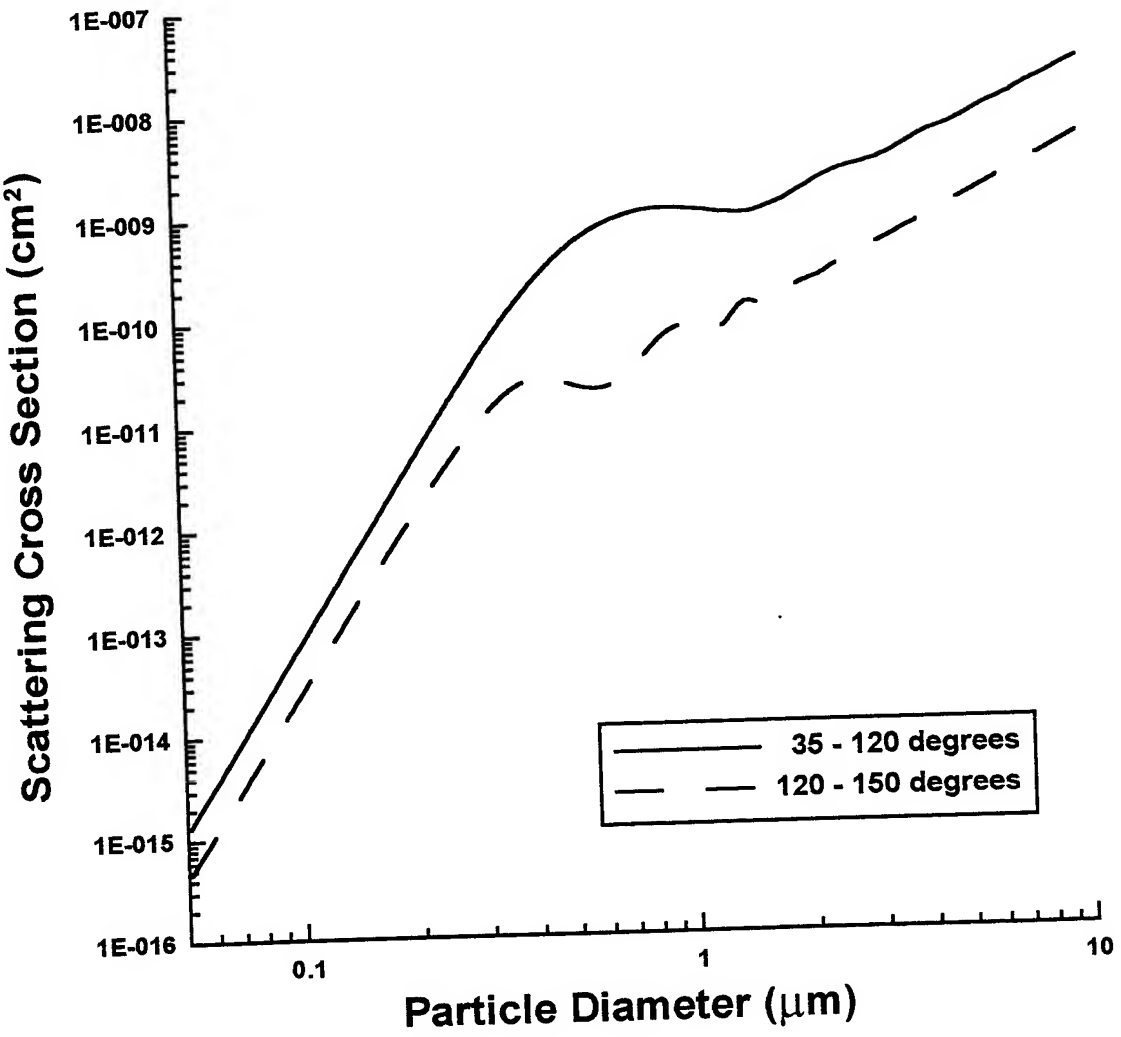


Figure 12

Theoretical scattering cross section as a function of particle diameter and the light collection angle. The dashed curve is the collection angle presently implemented in the AVS, and the solid line is the improvement that can be gained by using improved optics.

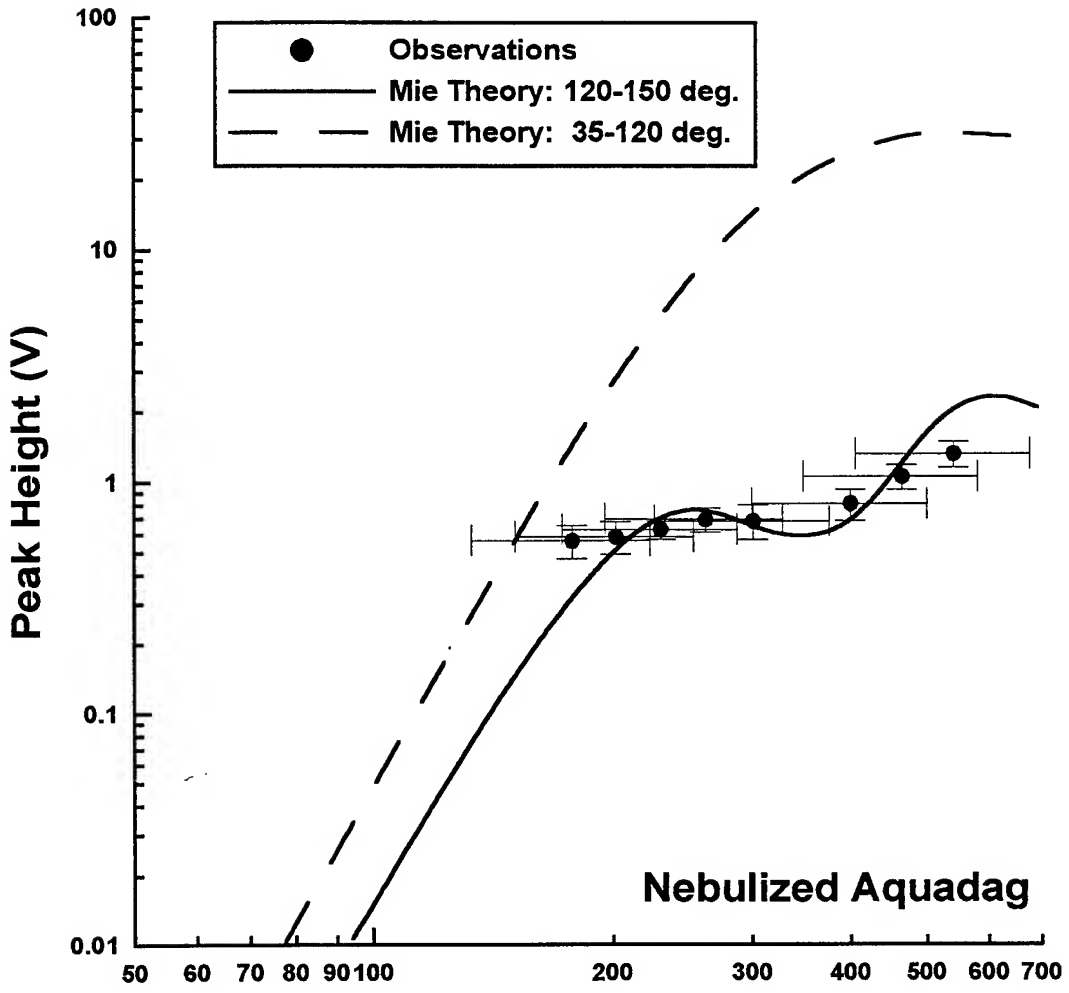


Figure 13

Expected scattering response from the AVS using the Mie scattering data in Figure 7 and the light collection data in Figure 12.

3.3 Flow system

The current system for introducing aerosols into the laser beam uses a sheath flow to direct the aerosols. This nozzle system is a decade old and more efficient systems are now available that direct the particle stream more precisely. Greater precision in aerosol focusing will increase the vaporization efficiency and decrease the uncertainty in mass determination. A flow model will be used to determine the optimal flow parameters to achieve this efficiency, i.e. relative velocities of sheath and sample flow and nozzle diameter.

3.4 Data system development

This will be accomplished in two steps. A high speed National Instruments 4 channel data logging card in a PC will be used first to collect data. Software will store the traces of the scattering and incandescence signals and analyze the time traces for peak shapes and signal arrival times. The results from this analysis will be used to establish the necessary sample rates, sensitivity, and amplitude ranges of a specialized signal processing card that will be developed in the second step of the data system development. This signal processing card will be then integrated into the optical system to do produce the derived parameters that completely characterize each particle's size, mass, shape, and temperature.

3.5 Expanded composition determination

In addition to calibrations with soot, the AVS will be tested with other, atmospherically important absorbing particles. In particular, Every possible black carbon containing compound will be located and tested. This includes graphite (with and without ash), diesel soot, flame soot, gas engine particulates, tire material, ash from coal fired power plants. In addition, silicate and metal oxides such as iron, nickel, magnesium and vanadium will be tested. A flow tube will be set up where carbon containing particles can be mixed with gaseous components such as ozone, sulfur dioxide, nitrogen oxides, ammonia and hydrocarbons. These gas phase species will absorb on the carbon, and in some cases oxidize, and this will produce mixed phase particles. These will be tested for response and compared with the pure materials.

3.6 Field Testing

The AVS will be run at a field site in the US or in other locations where there are a wide range of air quality measurements being made. In particular, the AVS measurements will be compared against commercial soot measuring instruments. An ideal comparison opportunity will be with the EPA aerosol supersites that measure a wide variety of criteria pollutants and aerosols, including several techniques for the measurement of black carbon.